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S.G. Louie

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Steven G. Louie

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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EXCITED STATES IN ELECTRONIC STRUCTURE CALCULATIONS

STEVEN G. LOUIE

*Department of Physics, University of California at Berkeley, and
Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720
USA*

ABSTRACT

A first-principles quasiparticle approach to the electronic excitation energies in crystals and at surfaces is described. The quasiparticle energies are calculated within the GW approximation for comparison with photoemission and other spectroscopic experiments. Applications of the method to bulk semiconductors and the Si(111)2×1, Ge(111)2×1, and H/Si(111) surfaces are presented. In both cases, significant self-energy corrections arising from many-electron effects to the excitation energies are found. Using atomic positions from total energy minimization, the calculated excitation energies explain quantitatively the experimental spectra. This approach thus provides an *ab initio* means for analyzing and predicting results from spectroscopic probes.

1. Introduction

Understanding the electron excitation spectra of condensed matter such as those measured in photoemission experiments requires detailed knowledge of the electronic structure. Electron-electron interaction effects, moreover, often lead to a significant renormalization of the properties of the electrons from those of the independent-particle picture. Nevertheless, experimental spectra from spectroscopic measurements may often be understood in terms of excitation between quasiparticle states of the interacting electron system. In this paper, we give a brief review of a method¹ for calculating the quasiparticle energies from first principles and discuss several selected applications.

The method is based on an expansion of the electron self-energy operator to first order in the dressed electron Green's function and the dynamically screened Coulomb interaction with local field effects included. This is the so-called GW approximation.² *Ab initio* calculations using this approach have successfully explained results from optical, photoemission, scanning tunneling, and other spectroscopic measurements for a variety of systems including bulk crystals, surfaces, interfaces, and small clusters.³ Here we focus the discussion on the application to semiconductors and their surfaces. The calculated quasiparticle energies are in general accurate to within ~ 0.1 eV of experimental values. The predictive capability of the approach is of particular value in many studies. For example, it is found that self-energy corrections to surface-state energies and band dispersions are substantial

and that electron-hole (excitonic) interactions may play a significant role in the optical response of some surfaces such as the Si(111)2x1 surface.

2. Self-energy Green's Function Approach to Quasiparticle Energies

It is the transitions between the quasiparticle states which are measured in most spectroscopic experiments.² Exchange and correlation effects can significantly modify the quasiparticle properties from those calculated using one-electron theories. The neglect of these many-electron effects in standard band structure calculations in the past has often given rise to rather severe discrepancies between theory and experiment. For example, although state-of-the-art local density functional (LDA) calculations yield very accurate structural properties, the LDA eigenvalues fail to give accurate band gaps and related excited-state properties.¹ Typically, the minimum gap in bulk semiconductors is underestimated by 30 - 100% in comparison to experiment leading to the so-called "band gap problem" in semiconductors.

The quasiparticle properties of an interacting electron system may be obtained using a Green's function approach. The electron or hole energies and wavefunctions are given by²

$$[T + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r})]\psi(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E^{\text{qp}})\psi(\mathbf{r}') = E^{\text{qp}}\psi(\mathbf{r}) , \quad (1)$$

where T is the kinetic energy operator, V_{ext} the external potential due to the ions, V_H the average electrostatic Hartree potential, and Σ the electron self-energy operator respectively. The self-energy operator contains the effects of exchange and dynamical correlations. In general, it is nonlocal, energy-dependent, and nonHermitian with the imaginary part giving the lifetime of the quasiparticles.

In the GW approximation,² the self-energy operator is expanded to first order in the screened Coulomb interaction:

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int d\omega e^{-i\delta\omega} G(\mathbf{r}, \mathbf{r}'; E - \omega) W(\mathbf{r}, \mathbf{r}'; \omega) . \quad (2)$$

Here, G is the crystalline Green's function and W the dynamically screened Coulomb interaction. Our approach¹ is to make the best possible approximations for G and W , calculate Σ , and then obtain the quasiparticle energies. Inclusion of local fields in the screened Coulomb interaction is found to be crucial for obtaining accurate quasiparticle energies because the off-diagonal elements of the dielectric matrix in Fourier space distinguish the variations in screening properties at the different regions in the crystal.

Since the quasiparticle energies E_{qp} and wavefunctions ψ enter into G , the quasiparticle energies together with Σ and G must be obtained self-consistently. In practice, the electron Green's function is constructed initially using the LDA Kohn-Sham eigenfunctions and eigenvalues, and subsequently updated with the quasiparticle spectrum from Eq. (1). The dynamical response matrix used to construct the screened Coulomb interaction W is typically obtained in two steps. First, the static dielectric matrix is calculated as a ground-state property from the LDA. Second, the dielectric matrix is extended to finite frequencies using a generalized plasmon pole model employing exact dispersion and sum rule relations. To simplify further the

calculation, the self energy is calculated only for the valence electrons. The exchange and correlation interactions between the valence and core electrons are treated via a pseudopotential formulation with these effects included at the LDA level. This last approximation has been shown to be very accurate in general. The only exceptions are some selected gaps in a few semiconductors with unusually shallow and polarizable core states. For these cases, realistic core-valence interactions may be successfully included using a core-polarization potential.⁴

The present quasiparticle approach has been applied to a range of crystals including semiconductors, ionic insulators, and the simple metals. Accurate band gaps, optical transition energies, and photoemission spectra have been obtained. These calculations have also been extended to various surfaces, interfaces, superlattices, and clusters³ and to the study of pressure induced insulator-metal transitions.⁵ A first-principles approach is of particular importance to the latter group of applications since these systems are often experimentally less well-characterized. The validity of the GW approximation to the d-band metals and other highly correlated electron systems however remains an open subject at this time.

3. Band Gaps and Photoemission Spectra of Bulk Semiconductors

Table 1. Comparison of calculated band gaps (in eV) with experiment. Core polarization and relaxation effects are included for Ge, AlAs, and GaAs.

	LDA	Present Theory	Expt. ^a
diamond	3.9	5.6	5.48
Si	0.5	1.16	1.17
Ge	-0.26	0.73	0.74
GaAs	0.12	1.42	1.52
AlAs	1.28	2.01	2.24
LiCl	6.0	9.1	9.4

^aSee Refs. 1 and 4.

A major success of the quasiparticle method described in Sec. 2 has been its application to the *ab initio* calculation of the band gaps and excitation energies in semiconductors and insulators.¹ The calculated band gaps of some selected crystals are presented in Table 1 together with the experimental values and the LDA Kohn-Sham gaps. In general, the LDA gaps significantly underestimate the experimental values. Hartree-Fock calculations, on the other hand, usually overestimate the gaps by several folds because of neglect of electron correlations. As seen in Table 1, with the excitation energies properly interpreted as transition between quasiparticle states, the calculated quasiparticle gaps are in excellent agreement with experiment. The present results were obtained with only input being the atomic number of the constituent elements and the crystal lattice parameters. The use of a self-consistent crystal Green function and the

inclusion of local fields (the full dielectric matrix) and dynamical screening effects are all important factors in describing accurately the self-energy effects.

As mentioned above, core-valence interactions can sometimes affect the value of certain gaps in materials with very shallow and highly polarizable core states. In Table 1, the values for the minimum band gap of Ge, GaAs, and AlAs were calculated

4. Semiconductor Surfaces

In this section we describe the extension of the first-principles quasiparticle approach to semiconductor surfaces. We use, as examples, the (111)2×1 surface of Si and Ge and the H/Si(111) surface to illustrate some recent efforts⁸⁻¹⁰ in this area. To compare with experimental excitation spectra, we calculate also the quasiparticle energies associated with the surface states. The quasiparticle studies complement structural studies: Atomic coordinates obtained in total energy calculations are used as input for the calculation of the excitation energies.

The calculations are carried out using a repeated slab geometry. Typically, about a dozen layers of the crystal are used with a vacuum region equivalent to several layers separating the slabs. The surface structure is determined by minimizing the total energy in a self-consistent LDA *ab initio* pseudopotential calculation.

4.1. The Si(111) and Ge(111)2×1 Surfaces

The Si(111)2×1 surface is one of the most studied semiconductor surfaces both theoretically and experimentally. The reconstructed structure has an interesting π -bonded chain of surface atoms.¹¹ Its electronic structure is also quite intriguing. The surface-state band gap measured from optical processes¹²⁻¹⁴ appears to be significantly different from that measured in photoemission^{15,16} and tunneling experiments¹⁷ indicating that electron-hole (excitonic) interactions may be considerably larger at this surface than in the bulk.

Figure 2 shows the calculated minimal energy structure⁸ of Si(111)2×1 surface as compared with structural parameters determined from LEED¹⁸ and medium energy inelastic scattering (MEIS)¹⁹ measurements. z_i is the coordinate of the i th atom along the surface normal. The positions of the surface atoms agree very well with experiments¹⁸⁻²⁰ and with previous theoretical calculations.²¹ Another interesting feature of this surface is that there is a rather large buckling of the surface chain atoms.

The surface electronic structure of Si(111)2×1 is dominated by a pair of π and π^* bands of surface states.⁸ These surface bands arise from the dangling bonds on the 3-fold coordinated surface atoms and are dispersive only along the chain direction resulting in one-dimensional-like bands. Figure 3 compares the calculated quasiparticle surface-state energies with angle-resolved direct¹⁵ and inverse¹⁶ photoemission data. Both the position and the dispersion of the surface states are given accurately by the quasiparticle theory. The overall agreement between theory and photoemission experiment is better for the occupied surface states than for the empty states which have larger experimental error bars. A subsequent analysis of the effects of the limited resolution in the inverse photoemission experiment¹⁶ indicates that the true energy of the π^* state at \bar{J} could be lower than that indicated in Fig. 3 by as much as 0.15 eV yielding a surface band gap in good agreement with the theoretical value of 0.62 eV. (The LDA surface-state gap is only 0.27 eV for this surface.) Scanning tunneling spectroscopy¹⁷ also gives an direct surface energy gap of 0.6 eV in agreement with our theoretical prediction. However, the measured onset energy¹²⁻¹⁴ for electron-hole creation is significant smaller than the calculated quasiparticle

surface-state gap. (See Fig. 4.) At low temperature, the optical gap is measured¹³ to be only 0.47 eV in significant disagreement with theory and with photoemission and tunneling results. Also observed is that there is only one asymmetric peak in the experimental optical absorption spectrum which is quite different from a two-peak structure predicted by the joint quasiparticle density of states of the π and π^* bands.

The situation with the Ge(111)2 \times 1 surface is very similar to that of the Si(111)2 \times 1 surface. The calculated quasiparticle surface-state energies⁹ show good agreement with results from direct and inverse angle-resolved photoemission experiments. For the surface-state band gap, a value of 0.65 ± 0.2 eV is inferred from combined direct²² and inverse²³ photoemission results, and a value of 0.65 eV is obtained from scanning tunneling spectroscopy.¹⁷ These values are in accord with our theoretical value of 0.67 eV. On the other hand, optical measurements from undoped samples^{24,25} and direct photoemission from heavily n-doped (to occupy the surface conduction states) samples²⁶ appear to give a band gap around 0.5 - 0.55 eV. This difference between the surface band gap measured by optical processes and that by single-particle processes is very similar to the situation in Si(111)2 \times 1. There is an added complexity in the case of the Ge(111)2 \times 1 surface. The energy minimum corresponding to the buckled chain geometry is much more shallow than that of the Si case. Since the surface-state band gap is quite sensitive to the amount of buckling,^{9,27} any theoretical uncertainty in this structural parameter would lead to a change in the gap value.

The observed discrepancies in the quasiparticle and the optical gap indicate that there may be enhanced excitonic effects^{8,28} of order of 0.1 eV in the surface optical data. This possibility has been suggested because of the quasi-1D dispersion

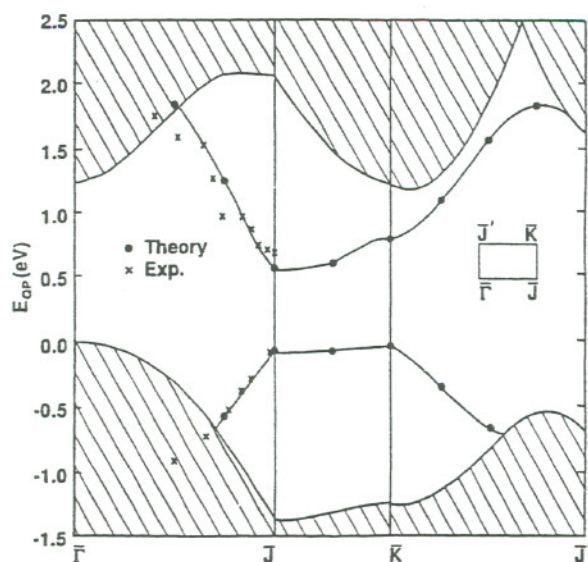


Fig. 3. Quasiparticle surface-state bands of Si(111)2 \times 1 compared to photoemission (Ref. 15) and inverse photoemission (Ref. 16) data.

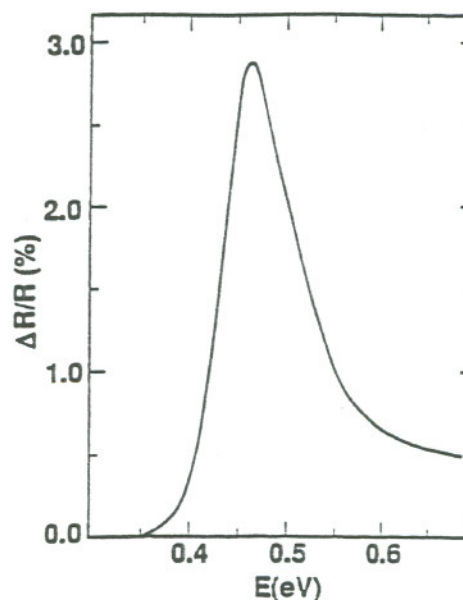


Fig. 4. Experimental differential reflectivity spectrum for the Si(111)2 \times 1 surface (after Ref. 13).

and reduced screening of the surface states of this particular surface. We performed a model calculation to estimate the effects of the electron-hole interaction. The exciton energy spectrum and wavefunctions were obtained within a model which employs the calculated surface-state quasiparticle bands and a model statically screened electron-hole interaction.^{8,29}

Figure 5 depicts the calculated $\alpha(E)$ for the Si(111)2 \times 1 surface for light polarized along the chains. Curve (b) corresponds to a complete neglect of the electron-hole interaction. In this case, $\alpha(E)$ exhibits two peaks corresponding to the critical points in the joint density of states. Curve (a) is that from an excitonic spectrum for which the lowest energy exciton had a binding energy of 0.13 eV obtained with a electron-hole Coulomb interaction screened by a dielectric constant taken to be 6.5. The absorption spectrum is dominated by the ground-state exciton, and the spectrum exhibits a single asymmetric peak. The large shift in oscillator strength as the electron-hole interaction is included is a result of both the reduced screening and the one-dimensional nature of the electronic structure near the edge ($\bar{J} \bar{K}$) of the surface Brillouin zone. The experimental differential reflectivity, which is closely related to $\alpha(E)$, has been measured by Ciccacci *et al.*¹³ and is shown in Fig. 4. It is clear that the absorption spectrum obtained by neglecting the electron-hole interaction cannot explain the data. Spectrum (a) in Fig. 5 which corresponds to an exciton binding energy of 0.13 eV, on the other hand, reproduces quite well the experimental value.

It should be emphasized that the calculated quasiparticle energies correspond to the energy needed to create an isolated electron or hole in the solid. Thus, it is consistent that these energies describe well the photoemission and tunneling data but not necessarily the optical data unless electron-hole interaction effects are small.

4.2. The H/Si(111)1 \times 1 Surface

The recent development of a chemical method³⁰ for preparing ideally hydrogen terminated Si(111) surfaces which are highly stable and easily transportable has renewed great interest in this system. Because of their structural perfection over large areas, remarkably sharp features in the valence and core level photoemission spectra have been obtained.¹⁰ The surface states on this surface have been examined in several calculations.^{31,32} However, discrepancies in their energies and dispersions as large as 1 eV were found between previous theories and experiment. We find that a quantitative understanding of the electronic structure requires a full quasiparticle calculation even for this simple chemisorption system.

From total energy minimization, the Si-H bond length is found to be 2.87 a.u. with the first silicon layer slightly relaxed inward while the relaxations of the deeper layers are negligible. Figure 6 depicts the calculated quasiparticle surface-state bands as compared to those from LDA calculation as well as the measured surface-state bands from photoemission.¹⁰ Well-defined surface states are found in each local gap of the projected band structure near K and M. Comparison of the LDA results to the quasiparticle energies reveal two important features. First, the self-energy corrections to the LDA surface-state energies are exceptionally large: the 0.76 eV correction for the level (a') at M is larger by a factor 2 to 3 as compared to typical previous self-energy corrections on occupied surface states.^{8,9} This is related to the

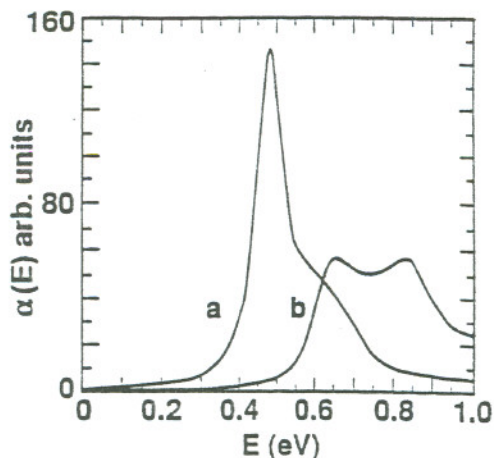


Fig. 5. Calculated surface-state optical absorption spectra obtained (a) with and (b) without excitonic correlations.

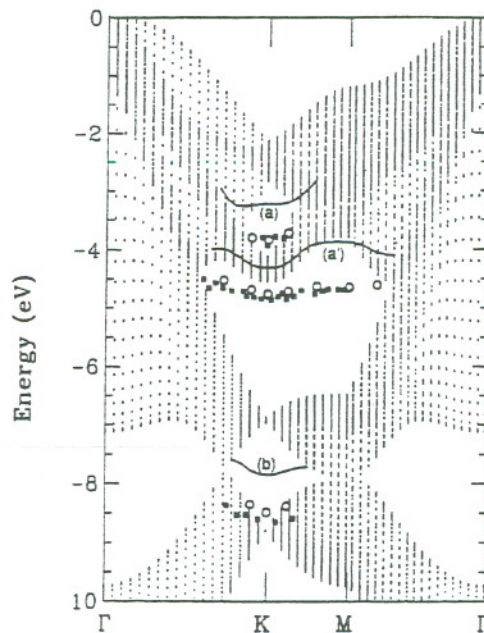


Fig. 6. Calculated surface-state bands of H/Si(111): LDA (full lines) and GW (open circles). The photoemission data (black dots) are from Ref. 10.

very localized hydrogen $1s$ orbital forming the surface states in the present system. Second, the self-energy effects give rise to a sizable correction to the band dispersion of the surface states. In particular, the LDA surface state band (a') shows a 0.42 eV dispersion going from M to K which does not appear in the experimental data. This discrepancy is completely removed in the quasiparticle self-energy formalism. This again may be understood from the sensitivity of the nonlocal self-energy operator to the localization of the electron wavefunction. The surface state (a') is much more localized at M than at K.

Figure 6 shows that the agreement between the present theory and experiment is excellent, including the location of the pockets in the projected bulk density of states. The self-energy approach yields an impressive improvement in the energy location and dispersion of all the surface states. Even the state (a') at K, which in the LDA treatment is a surface resonance, is successfully extracted by the self-energy operator from the continuum of bulk states.

5. Summary

We have described in this brief review a first-principles method for calculating the quasiparticle energies in solids. Several recent studies are presented to illustrate the applicability of this approach to the excited-state properties of semiconductors and their surfaces. Specific examples discussed include the bulk crystals and the Si(111)2×1, Ge(111)2×1, and the H/Si(111) surfaces. In general, agreement to within

~ 0.1 eV is achieved between the calculated results and data from optical, photoemission, scanning tunneling, and other spectroscopic measurements. Self-energy corrections to standard self-consistent field theories such as the LDA or Hartree-Fock methods are shown to be quite substantial for both bulk and surface systems. It is also found that electron-hole (excitonic) interactions play an important role in the optical response of some surfaces such as the Si(111) 2×1 surface.

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